



Short communication

Ti- and Zr-based metal-air batteries

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HIGHLIGHTS

- A high-temperature Ti or Zr-air battery that shuttles oxygen is proposed.
- A first-principles study predicts a high capacity and voltage for this battery.
- Ti and Zr dissolves oxygen topotactically up to 33% and remains metallic.
- Oxygen is predicted to have a high mobility in TiO_x and ZrO_x at elevated temperature.

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ABSTRACT

We propose a high-temperature, rechargeable metal-air battery that relies on Ti or Zr metal as the anode and the shuttling of oxygen anions between the cathode and the anode through a solid-oxide ion-conducting electrolyte. The cathode has much in common with solid-oxide fuel cells. Key in the proposed battery is the use of Ti or Zr as the anode as these metals are unique in their ability to dissolve oxygen up to concentrations of 33% with minimal structural and volumetric changes. First-principles statistical mechanics calculations predict open circuit voltages around 2.5 V, substantially larger than the open circuit voltage of high-temperature solid-oxide fuel cells. The calculations predict the stability of TiO and ZrO monoxides along with TiO_x and ZrO_x (with x as high as $\frac{1}{2}$) solid solutions. These suboxide phases are all predicted to be metallic, indicating that electron transport in the anodes will not be rate limiting. The oxygen diffusion coefficients in the Ti and Zr suboxides at high temperature ($\sim 700\text{--}800^\circ\text{C}$) are predicted to be comparable to that of Li ions in intercalation compounds. These properties suggest theoretical capacities as high as 840 mAh g^{-1} and 500 mAh g^{-1} for Ti and Zr based metal-air batteries respectively.

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1. Introduction

The use of intercalation compounds as electrodes in Li-ion batteries has proven crucial to the success of these electrochemical storage devices, enabling high charge and discharge rate capabilities as well as high cycle lifetimes. Li-intercalation compounds used as electrodes in Li-ion batteries consist of an electronically conducting host structure that can undergo large variations in Li concentration without significant crystallographic modifications [1,2]. A drawback of intercalation compounds, however, is their limited capacity, both by weight and volume. Alternative electrode reaction mechanisms are, therefore, actively investigated [3–10]. One such mechanism, inspired by the Li-air

battery [3,6,9], is to dispense of the host structure altogether and to let the shuttled ion react with oxygen in ambient air, thereby forming a metal oxide at the cathode (i.e. Li_2O_2 or Li_2O in the Li-air battery). Although the theoretical capacity of a Li-air battery is substantially higher than can be achieved with intercalation compounds, it nevertheless suffers from sluggish kinetics and large hysteresis between charge and discharge [6,9]. This poor kinetics has its origin in part due to the formation of the electronically insulating and poorly conducting oxide reaction product on the current collector. The Li-air battery has nevertheless sparked interest in other metal-air battery concepts. The challenge there, however, is the difficulty in finding electrolytes that conduct multivalent metal cations.

Here we propose a high-temperature metal-air battery that has much in common with intercalation processes, relying on pure Ti or Zr as the anode. The proposed battery is similar to the high-temperature battery recently developed at CIC EnergiGune [11],

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which shuttles oxygen anions instead of metal cations. Instead of using low melting temperature metals as the anode as in Reference 11, we propose solid Ti or Zr as the anode. We will refer to this type of battery as an oxygen-shuttled metal-air (OSMA) battery. Using first-principles electronic structure calculations, we confirm that Ti and Zr have unusually high oxygen solubilities in the solid state [12–22], remain metallic upon oxygen insertion up to this solubility limit and undergo minor structural and volumetric changes as the concentration of dissolved oxygen is varied. Furthermore, we predict this high-temperature battery to have an open circuit voltage and an oxygen anion mobility (within the anode) that is comparable to that of Li-ion batteries (albeit it at solid-oxide fuel cell operating temperatures).

2. Battery design

A schematic of the proposed battery is illustrated in Fig. 1. The battery consists of (i) a metal anode, (ii) an electrolyte that only allows oxygen ions to pass through but is electronically insulating and (iii) a cathode that is a reservoir containing oxygen gas at a fixed partial pressure. The cathode side of the battery is identical to a high-temperature solid-oxide fuel cell, where a catalyst is needed to dissociate oxygen molecules O_2 into two oxygen anions O^{2-} . A key component of the proposed battery is the use of either Ti or Zr metal as the anode, which are able to dissolve oxygen anions topotactically [20–22] as occurs in Li-ion batteries relying on intercalation compounds. Similar to an intercalation process, oxygen inserts into the hcp crystal structure of the Ti or Zr anode and diffuses to the interior of the metal, thereby raising the overall oxygen concentration of the metal. The anode oxide ion concentration increases during discharge until its oxygen solubility limit is reached, which for Ti and Zr is $\sim 33\%$.

We first derive a Nernst equation to link the open circuit voltage of this battery to oxygen chemical potentials in the anode and cathode. At open circuit, the battery will reach an equilibrium state at constant temperature and pressure. Hence equilibrium is determined by the minimization of the Gibbs free energy of the battery with respect to internal degrees of freedom. These free to vary degrees of freedom include the concentrations of oxygen in the anode and cathode as well as the concentration of excess electrons within the two electrodes.

$$dG = \mu_{O_2}^c dN_{O_2}^c + \mu_e^c dN_e^c + \phi^c dq^c + \mu_O^a dN_O^a + \mu_e^a dN_e^a + \phi^a dq^a$$

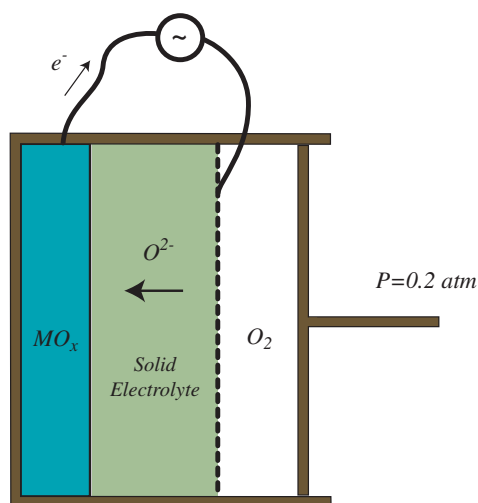


Fig. 1. Schematic of a metal-air battery in which oxygen is shuttled between cathode (air) and a metal anode with a high oxygen solubility ($M = \text{Ti or Zr}$).

In this expression, the superscript “c” (“a”) refers to cathode (anode), the “ μ ”s are chemical potentials and the “ ϕ ”s are electrostatic potentials within the electrodes. “ N ” denotes the number of atoms or electrons and “ q ” denotes the charge. The subscript “O” refers to oxygen, “ O_2 ” to an oxygen molecule and “e” to electron. The electron chemical potential, μ_e^a , corresponds to the Fermi level in the anode. Only one of the differentials in the above expression for dG is independent due to mass and charge conservation. For convenience, we take $N_{O_2}^c$ as the independent variable such that $dN_O^a = -2 dN_{O_2}^c$, $dN_e^c = -4 dN_{O_2}^c$, $dq^c = -e dN_e^c = 4e dN_{O_2}^c$, $dN_e^a = 4 dN_{O_2}^c$ and $dq^a = -e dN_e^a = -4e dN_{O_2}^c$. Substituting these in the differential form of the Gibbs free energy and setting it equal to zero yields:

$$dG = (\mu_{O_2}^c - 4\mu_e^c + 4e\phi^c - 2\mu_O^a + 4\mu_e^a - 4e\phi^a) dN_{O_2}^c = 0$$

or equivalently:

$$\mu_{O_2}^c - 4\eta_e^c - 2\mu_O^a + 4\eta_e^a = 0$$

where we have introduced the electron electrochemical potential $\eta_e = \mu_e - e\phi$

The electromotive force when the battery is in open circuit is equal to the difference in electron electrochemical potential across the cathode and anode according to:

$$\text{emf} = -(\eta_e^c - \eta_e^a)/e = -(\mu_{O_2}^c/2 - \mu_O^a)/2e$$

Hence, the electromotive force is determined by a difference in oxygen chemical potentials across the electrodes of the battery. First-principles statistical mechanical approaches allow us to predict the variation of the oxygen chemical potentials as a function of anode oxide ion concentration and the oxygen partial pressure in the cathode.

3. Methodology

We used a combination of first-principles electronic structure calculations (density functional theory) within the generalized gradient approximation (PBE) as implemented in the Vienna ab initio Simulation Package (VASP, University of Vienna, Austria) [23–26] and statistical mechanics methods to calculate relevant electronic, thermodynamic and kinetic properties of the Ti–O and Zr–O binary systems. This approach has been used extensively in the study of Li-intercalation compounds [27–33]. We accounted for the configurational degrees of freedom associated with the many possible ways of distributing oxygen and vacancies over the interstitial sites of hcp Zr and Ti with the cluster expansion formalism [34,35]. Combined with Monte Carlo simulations, this approach enables the prediction of finite temperature phase stability of ordered and disordered phases, of thermodynamic potentials (free energies and chemical potentials) as well as diffusion coefficients. For the chemical potential of oxygen gas appearing in the above Nernst equation, we used thermodynamic data from the NIST Standard Reference Database [36] with a shift due to [37] to eliminate systematic errors inherent to approximations to density functional theory when going from the gas state (molecular O_2) to the solid state (oxygen dissolved in Zr and Ti).

4. Results

Fig. 2 shows the calculated voltage curves of a ZrO_x and TiO_x based OSMA battery at 300 K and 900 K. The plateaus in the voltage curve are due to two-phase regions and the steps are due to the

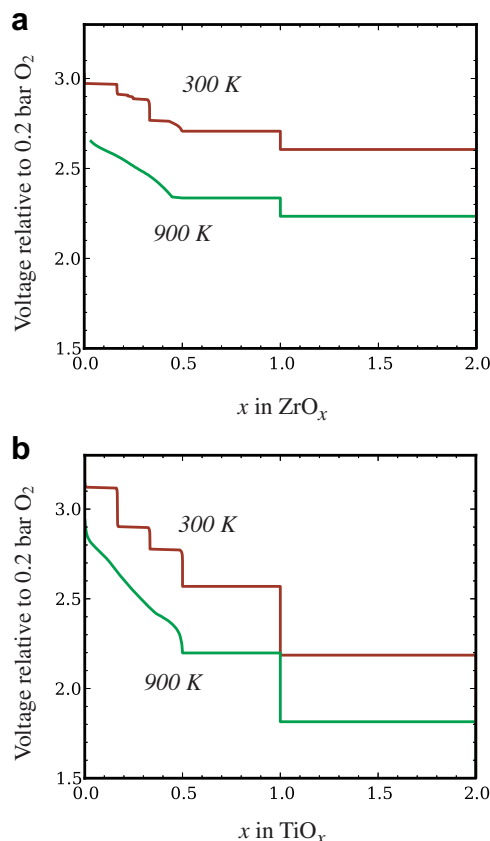


Fig. 2. First-principles calculated voltage profiles of (a) a ZrO_x and (b) a TiO_x (anode) based oxygen-shuttling metal-air (OSMA) battery. The plateaus at 300 K arise from two-phase regions and the steps are due to the stability of the ordered phases: $\text{ZrO}_{1/6}$, $\text{ZrO}_{1/3}$, $\text{ZrO}_{1/2}$ and ZrO and equivalently $\text{TiO}_{1/6}$, $\text{TiO}_{1/3}$, $\text{TiO}_{1/2}$ and TiO .

stability of ordered phases at stoichiometric oxygen concentrations. The first ordered phase upon oxygen insertion at low temperature into hcp Zr is a staged phase, having a stoichiometry of $\text{ZrO}_{1/6}$, with the oxygen ordering on a $\sqrt{3}a \times \sqrt{3}a$ supercell in alternating (0001) planes of octahedral interstitial sites. Further oxygen insertion results ultimately in the filling of the empty layers to form $\text{ZrO}_{1/3}$ followed by a gradual transition to $\text{ZrO}_{1/2}$, both also having a $\sqrt{3}a \times \sqrt{3}a$ supercell in the (0001) basal plane [20–22]. At higher temperature (900 K), the ordered phases are no longer thermodynamically stable and are replaced by a solid solution. This results in a more sloping voltage profile as illustrated in Fig. 2. Oxygen insertion into hcp Ti follows almost an identical sequence of ordered phases, the most important having stoichiometries $\text{TiO}_{1/6}$, $\text{TiO}_{1/3}$ and $\text{TiO}_{1/2}$. The insertion of oxygen into hcp Zr and Ti is very similar to Li insertion into graphite or other layered intercalation compounds such as Li_xTiS_2 and Li_xCoO_2 , which also exhibit phases having $\sqrt{3}a \times \sqrt{3}a$ in plane Li ordering and undergo staging reactions [1,29,38–42].

First-principles electronic structure methods, in addition to predicting thermodynamic properties, also provide crucial insight about electronic properties. Remarkably, the hcp based ZrO_x and TiO_x phases are predicted to be metallic, an important property for electrode materials. For example, calculated electronic density of states for three stable ordered phases $\text{ZrO}_{1/6}$, $\text{ZrO}_{1/3}$ and $\text{ZrO}_{1/2}$ all have the Fermi level cutting through Zr d-bands having a high electronic density of states. This implies that there should be sufficient charge carriers for electron transport and that hcp Zr with dissolved oxygen should behave like a metal. Similar electronic structure properties are predicted for the Ti–O system.

Another unique property of the substoichiometric ZrO_x and TiO_x oxides is their minimal volume change as a function of oxygen concentration. We found that the volume change between Zr (Ti) and the various stable suboxide phases having different oxygen-vacancy configurations over the octahedral sites of hcp Zr (hcp Ti) is less than 3.15% (6.36%). This suggests that electrode degradation due to repeated swelling and contraction during discharge and charge should be minimal.

The theoretical capacities of the Ti–O and Zr–O electrodes, while less than that of Li–air, are higher than Li-batteries relying on intercalation processes. Our calculations of theoretical capacity are based on the final weight of the metal anode and assume a maximum anode oxide ion content of $\text{MO}_{1/2}$. One mole of $\text{TiO}_{1/2}$ has a weight of 55.8667 grams. There are $26801.48 \text{ mAh mol}^{-1}$ of electrons. There is 1 mol of e^- per mol of $\text{TiO}_{1/2}$, because there are $2e^-$ per mol of O and $1/2 \text{ mol}$ of O in the fully discharged anode. The capacity is therefore: $26801.48/55.8667 = 480 \text{ mAh g}^{-1}$. Similarly for the Zr–O electrode going to $\text{ZrO}_{1/2}$, the theoretical capacity is 270 mAh g^{-1} .

Our comprehensive first-principles studies of phase stability in the Ti–O and Zr–O systems predict the stability of monoxides (ZrO and TiO) with volumes that are larger than the original unoxidized metallic phases, but not by the extremes of typical oxidation or conversion type of reactions ($\text{Ti} \rightarrow \text{TiO}_{1/2}$: 6.36%; $\text{Ti} \rightarrow \text{TiO}$ 20.79%; $\text{Zr} \rightarrow \text{ZrO}_{1/2}$: 3.15%; $\text{Zr} \rightarrow \text{ZrO}$: 11.99%). Furthermore, the monoxides are metallic indicating that the formation of these monoxides should not dramatically reduce electronic conductivity. Nevertheless, they have a different Ti and Zr sublattice (no longer hcp, but rather based on the ω phase) [22]. Insertion of oxygen to form TiO and ZrO is therefore not topotactic and requires a change in crystal structure. While at high temperature, this may occur readily, usually a change in crystal structure is undesirable as it leads to increased dissipation (hysteresis between charge and discharge) and is usually an underlying cause of degradation. If, however, the formation of the monoxides at high temperature is facile and reversible, the theoretical capacities of these metals would be almost double those of the above values (i.e. 840 mAh g^{-1} for Ti and 500 mAh g^{-1} for Zr based on the weight of TiO and ZrO respectively). We point out though that the monoxides are predicted to be stable at zero Kelvin and that no finite temperature analysis of phase stability was performed for these phases.

Rapid charge and discharge requires high ionic mobilities, not just in the electrolyte, but also within the electrodes. It is also possible to predict diffusion coefficients from first-principles [28, 29]. Insertion of oxygen into the octahedral sites of hcp Zr and Ti results in non-dilute diffusion, as the oxygen concentration increases upon discharge. Oxygen diffusion in hcp Ti and Zr is complex even in the dilute limit, with several competing hop pathways between adjacent octahedral sites. Both our own first-principles analysis on Zr, using kinetic Monte Carlo simulations, and an analysis by Wu and Trinkle [43] on Ti, predict that the oxygen diffusion coefficient in the dilute limit at 800°C is of the order of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Furthermore, a preliminary calculation of the oxygen diffusion coefficient as a function of oxygen concentration combining kinetic Monte Carlo simulations with a cluster expansion indicates that the chemical diffusion coefficient only varies within an order of magnitude with oxygen concentration. A value of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ is comparable to, but on the low end, of currently used Li-intercalation compounds at room temperature.

5. Discussion

The crystallographic, electronic, thermodynamic and kinetic properties associated with the insertion of oxygen into the interstitial sites of hcp Zr and Ti are remarkably similar to that of Li

insertion into common intercalation compounds used in Li-ion batteries. This therefore motivates the use of these hcp elemental metals as anodes in an oxygen-shuttled, metal-air battery. In contrast to Li-batteries, though, the electrochemical insertion of oxygen into Zr and Ti must occur at high temperature to achieve sufficiently high oxygen diffusion coefficients. High temperatures are also necessary for high oxygen mobility within the solid electrolyte and for the dissociation of oxygen molecules at the cathode side of the battery. The temperature, though, cannot exceed the hcp-bcc transition temperatures of Ti and Zr ($\sim 880^\circ\text{C}$) since the oxygen solubility in the bcc crystal structure is much lower. The dissociation of oxygen molecules at the cathode would require a catalyst just as in a solid-oxide fuel cell. While similar to a fuel cell in many ways, this metal-air battery has a predicted EMF that is almost three times higher than that of a solid-oxide fuel cell. Furthermore, it cannot be run continuously since the anode has a finite capacity before the battery needs to be recharged. In spite of having finite capacities, these high-temperature air batteries boast higher theoretical capacities than Li-ion batteries relying on intercalation processes (as much as 840 mAh g^{-1} for Ti-air and 500 mAh g^{-1} for Zr-air). Compared to other metal-air batteries, the minimal structural and electronic changes upon oxygen insertion into Ti and Zr along with reasonable oxygen diffusion coefficients at high temperature should make it highly likely that capacities close to the theoretical values can be achieved.

A crucial component of this metal-air battery is a suitable choice for the solid electrolyte. An obvious candidate would be yttria-stabilized zirconia (YSZ) due to its proven track record in solid-oxide fuel cells. An important property in any battery is electrolyte stability. Several factors determine electrolyte stability. The electrolyte must be electronically insulating in the voltage range of the battery. Furthermore, it should be thermodynamically stable when it is in contact with the elements of the anode and cathode. In this respect, a Zr-air battery with a YSZ solid electrolyte can be viewed as a heterostructure in a ternary composition space spanned by Zr-Y-O. Phase stability in this ternary composition space is well characterized [44]. The high-temperature ternary Zr-Y-O phase diagram as assessed by Chen et al [44] already suggests that solid-solutions of hcp Zr with dissolved oxygen form tie-lines with Y_2O_3 and not with YSZ. This implies that if ZrO_x is originally in contact with YSZ, as would be the case at the anode/electrolyte interface, the interface between Zr and YSZ will be thermodynamically susceptible to decomposition. In view of the tie-lines between ZrO_x and Y_2O_3 in the Zr-Y-O phase diagram [44], one possible electrode-electrolyte reaction could involve decomposition of YSZ in contact with the Zr anode into Y_2O_3 with excess Zr and oxygen from YSZ entering the anode to form more $\text{ZrO}_{1/2}$. This is schematically illustrated in Fig. 3. However, if cation mobility within YSZ is sufficiently low, this decomposition may be suppressed kinetically. Whether or not this happens should be established experimentally. Many other oxygen conducting solid electrolytes exist and undoubtedly some of these will not have a tendency to react with ZrO_x or TiO_x .

In addition to showing promise as a high-temperature metal-air battery, the Ti and Zr-air batteries can also serve as a model electrochemical system to experimentally study electrode-electrolyte interactions and electrolyte breakdown. The fact that battery operation must occur at high temperature allows electrode-electrolyte interface evolution to be quenched in, thereby facilitating detailed chemical and structural ex-situ characterization. The high volatility of additives and organic electrolyte components coupled with rapid room temperature kinetics have proven very challenging for a satisfactory characterization of the mechanisms of electrolyte breakdown and solid-electrolyte-interphase formation in Li-ion batteries. Furthermore, current Li-ion batteries consist of a large number of components when considering the cathode,

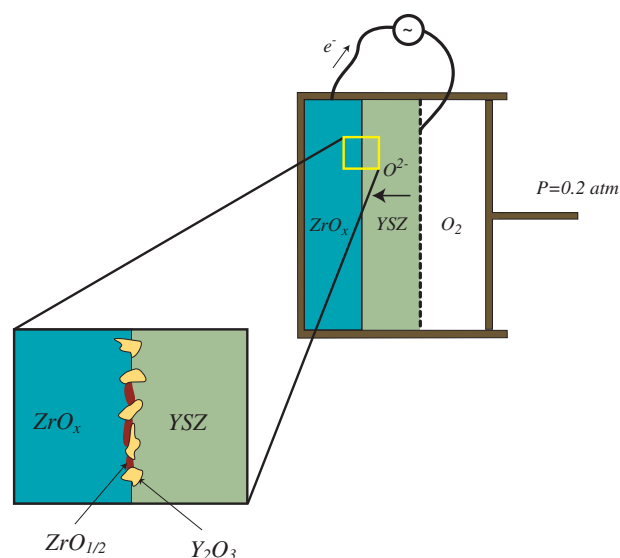


Fig. 3. Schematic illustration of possible electrolyte decomposition reactions when ZrO_x is in contact with YSZ. According to the ternary Zr-Y-O phase diagram at high temperature [44], hcp ZrO_x is not in thermodynamic equilibrium with YSZ, but rather with Y_2O_3 . Whether this decomposition actually occurs will depend on the mobilities of Y and Zr in YSZ.

electrolyte and anode as one thermodynamic system. This makes the task of rigorously analyzing the thermodynamic stability of the cathode/electrolyte/anode heterostructure an almost impossible task. In contrast, the proposed Zr and Ti-air batteries as a system contain a very limited number of species (three species for Zr-air when using YSZ and four species for the Ti-air battery when using YSZ). A full characterization of phase stability in ternary and quaternary systems is both experimentally and computationally quite feasible. Experimental characterization of electrolyte stability and the formation of the equivalent of a solid-electrolyte interphase (SEI) will then indicate whether the electrolyte decomposition products are thermodynamically stable phases or whether they are completely unsuspected phases formed due to kinetic factors or thermodynamic factors that are usually ignored such as the presence of high electric fields at electrode/electrolyte interfaces.

6. Conclusion

Both Ti and Zr in the hcp crystal structure exhibit a range of thermodynamic, kinetic and structural properties that make them ideal candidates as anodes for oxygen-shuttled metal-air batteries. They both dissolve oxygen topotactically up to a composition of $\text{TiO}_{1/2}$ ($\text{ZrO}_{1/2}$) with minimal volume change. The Ti-O and Zr-O hcp based solid solutions are predicted to have metallic electronic properties. The capacities are respectable: 480 mAh g^{-1} for Ti and 270 mAh g^{-1} for Zr. These capacities can almost be doubled if discharged to TiO and ZrO stoichiometries, however, then oxygen insertion is no longer topotactic (nevertheless TiO and ZrO are also metallic and have volumes that are not too different from that of hcp Ti and Zr). The oxygen diffusion coefficient at 800°C is predicted to be of the order of $10^{-12}\text{ cm}^2\text{ s}^{-1}$, which is comparable to Li diffusion coefficients in intercalation compounds (though on the low end).

Acknowledgments

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